force of terrestrial magnetism, have electric currents circulating in them.

The difficulty against this supposition always seemed to me to lie in the fact that the electromotive forces required to start a current were larger than those which could possibly exist in the atmosphere. But as there are very likely continuous electric disturbances going on, such as we observe in auroræ and thunderstorms, the regions within which these discharges take place would act as conductors for any additional electromotive force however small, so that any regular motion, such as tidal motions, could very well produce periodic effects affecting our magnetic needles.

If these original discharges increase in importance, then, according to the results obtained in this paper, the currents due to the smaller periodic causes would increase also, and they may increase in a very rapid ratio. We know that the electric discharges in the upper regions of the atmosphere are considerably stronger at times of many sunspots, and this may account for the fact that at those times the amplitude of the daily oscillation of the magnetic needle is considerably increased.

I have had considerable assistance in these experiments from my assistant, Mr. Stanton, to whom my best thanks are due.

XI. "Contributions to our Knowledge of Antimony Pentachloride." By Richard Anschütz and P. Norman Evans. Communicated by Prof. A. W. Williamson, For. Sec. R.S. Received May 5, 1887.

Some months ago* we showed that antimony pentachloride can be distilled, undecomposed, under much diminished pressure; our next step was the attempt to determine the vapour-density under similar conditions. The fact that the boiling point of antimony pentachloride lies much lower than that of the trichloride would seem to show that the vapour-density of the pentachloride, as in the case of the trichloride, corresponds to the simpler formula. Nevertheless, on account of the fundamental importance which the establishment of the simple formula $SbCl_5$ would have for the valence of antimony, it seemed indispensably necessary to make a determination of the vapour-density. We will preface our further observations with the remark that we have not yet succeeded in determining the vapour-density of antimony pentachloride under diminished pressure; however, in the course of many unsuccessful attempts which we have made to this end, we had one point thrust on our notice, which on

* 'Chem. Soc. Journ.,' vol. 49, 1886, p. 708.

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investigation led to some important results concerning our knowledge of the chemical nature of antimony pentachloride.

Antimony pentachloride is well known to be an extremely hygroscopic body. Consequently in the application of La Coste's modification of Victor Meyer's method for the determination of vapour-densities under diminished pressure, it was necessary to substitute liquid paraffin for water; yet, in spite of numerous careful experiments, we could not attain our object, the liquid paraffin offered too great a resistance to the air, and before all the air had been driven out the antimony pentachloride distilled into the upper and cooler parts of the apparatus. During these experiments it was proved to us that it is next to impossible to prevent the formation of traces of the white substance, which is the result of the action of water on antimony pentachloride. We were accordingly constrained to put this method aside.

Before attempting the determination of antimony pentachloride by another method, we deemed it best first to find out the nature of the error caused by the formation of the minute amount of the product of water reacting on antimony pentachloride.

After careful consideration we were struck by the contradiction between the conclusions of Daubrawa* and those of R. Weber,† concerning the behaviour of antimony pentachloride with water. According to the latter, antimony pentachloride forms with water a hydrate, which is impossible if with 1 mol. of water antimony pentachloride is changed in the cold to $SbOCl_3$ and 2 mols. of hydrochloric acid, as Daubrawa thinks he has proved.

The following results of our experiments show that Daubrawa's statements concerning antimony oxychloride, $SbOCl_3$, are entirely wrong. In connexion with these studies we have occupied ourselves with the action of oxalic acid on antimony pentachloride, and have succeeded in obtaining the remarkable product of this reaction in a pure state.

Reaction of Water on Antimony Pentachloride.

Daubrawa allowed 1 part by weight of distilled water to drop from a pipette into a flask, surrounded by ice, containing 16 parts by weight of antimony pentachloride. He found the decomposition accompanied by hissing, and by the formation of vapour, giving no white pulverulent precipitate, but forming a yellowish distinctly crystalline mass, which adhered to the flask. This crystalline mass, the behaviour of which with water Daubrawa describes in detail, is, according to his analysis, antimony oxychloride, $SbOCl_3$, and he expresses its formation from antimony pentachloride and water by the following equation:—

* 'Liebig's Annalen,' vol. 186, 1887, p. 118.

† 'Poggendorff, Annalen,' vol. 125, 1865, p. 86.

$$Sb\left\{\begin{matrix}Cl\\Cl\\Cl\\Cl\\Cl\end{matrix}\right. + H_2O = SbOCl_3 + 2HCl.$$

We proceeded exactly as above described, and joined to our flask a receiver containing a weighed quantity of water in which to collect the liberated hydrochloric acid. To 21·5 grams of well-cooled antimony pentachloride, which had been purified by distillation under diminished pressure, we added drop by drop 1·2 gram, the calculated amount, of water, and found to our surprise that no hydrochloric acid was liberated; also that the yellowish crystalline product was equal in weight to the sum of the weights of the water and antimony pentachloride originally taken.

The resulting product was only partly soluble in chloroform, and was therefore a mixture of different substances.

We therefore altered the conditions of the experiment. In order to moderate the reaction we dissolved 20·4 grams of pure antimony pentachloride in about the same volume of chloroform, and added drop by drop to the cooled solution the calculated amount, 1·1 gram, of water, shaking constantly. The formation of the new body was soon apparent by the separation of almost colourless crystals; the yellow colour of the chloroform, caused by the antimony pentachloride (which according to our experience is never colourless, but always a bright yellow liquid), gradually disappeared, and at the end of the reaction the crystals which had separated were covered by colourless liquid. Under these changed conditions there was again no trace of hydrochloric acid set free. We next heated our product nearly to the boiling point of chloroform, adding sufficient dry chloroform to dissolve the crystals which had separated. From this solution a compound was deposited in feathery crystals. After decanting the mother-liquor, these were washed with a small quantity of chloroform, and placed to dry in a vacuum desiccator on a porous plate that had been previously heated. This body is so extraordinarily hygroscopic that the analyses were not very easy; however, the results leave no doubt that $SbCl_5H_2O$ is the formula:—

1. 0·2719 gram	substance	gave	0·6074 AgCl.	
2. 0·1457	,,	,,	0·3270 AgCl.	
3. 0·1467	,,	,,	0·3290 AgCl.	
4. 0·3003	,,	,,	0·1461 Sb_2O_4.	
5. 0·3104	,,	,,	0·1492 Sb_2O_4.	
6. 0·2020	,,	,,	0·1061 Sb_2S_3.	
7. 1·1387	,,	,,	0·0961 H_2O	Combustion with lead chromate.
8. 1·3905	,,	,,	0·1180 H_2O	

	Calculated for $SbCl_5H_2O$.	Found. 1.	2.	3.	4.	5.	6.	7.	8.
Cl...	55·90	55·26	55·52	55·48	—	—	—	—	—
Sb ..	38·42	—	—	—	38·53	38·08	37·69	—	—
H...	0·63	—	—	—	—	—	—	0·93	0·94
O...	5·04								
	99·99								

We provisionally designate this body as antimony pentachloride monohydrate, without expressing any opinion concerning the constitution of this addition product of equal molecules of water and antimony pentachloride. From chloroform, the monohydrate crystallises in leafy or feathery crystals resembling sal-ammoniac, having a melting point lying between 87° and 92°. If exposed to the air it deliquesces to a clear liquid, which over sulphuric acid gradually crystallises again in broad needles, described by Daubrawa as a property of his supposed oxychloride. We have not further examined this body.

When one tries to distil the antimony pentachloride monohydrate under diminished pressure—under 20 mm. with the bath at 105°—a mobile yellow liquid distils over; this, after two rectifications, boiled constantly at 73° under 17 mm. (bath 90°). Two chlorine determinations gave, as was expected, results for antimony pentachloride.

1. 0·2510 gram substance gave 0·5965 AgCl.
2. 0·2879 ,, ,, 0·6885 AgCl.

	Calculated for $SbCl_5$.	Found. I.	II.
Cl	59·24	58·80	59·15

There separated from a fraction boiling somewhat higher crystals of antimony trichloride, leaving a residue of a waxy consistency which could not be distilled.

22·7 grams $SbCl_5H_2O$ gave 12·8 grams $SbCl_5$.
,, ,, 1·1 grams $SbCl_3$.
,, ,, 6·4 grams residue.
,, ,, 2·4 loss.

Although after this experience it was not probable that we could obtain antimony oxychloride, $SbOCl_3$, by heating antimony pentachloride monohydrate, we repeated the experiment in another form. We heated 24·4 grams of antimony pentachloride, mixed with about twice its volume of chloroform and 1·4 gram water, in a closed tube to 100° on a water-bath. The crystals of the monohydrate which

were first formed went into solution, and on opening the tube before a lamp at the end of six hours we found much pressure; a gas smelling like phosgene was liberated. The tube was again closed and heated afresh to 100°. The opening and closing was repeated, first at intervals of six hours, and later, as the pressure diminished, of twelve hours, until after about fourteen days the pressure was no longer noticeable.

On working up the products of the reaction we found, besides antimony tri- and penta-chlorides, *phosgene* in solution in the chloroform, from which we prepared diphenyl carbamide, m. p. 239°. For the formation of phosgene gas it is not necessary to work in closed tubes. A chloroform solution of the monohydrate, heated to its boiling point on a water-bath, yields a steady stream of phosgene mixed with hydrochloric acid. A similar decomposition takes place when carbon tetrachloride is heated with antimony pentachloride monohydrate in a closed tube to 100°. We will communicate the quantitative relations of this reaction after we have verified our first observations by repeated research.

One can make the tetrahydrate of antimony pentachloride even more easily than the monohydrate. For this purpose we dissolved 29·3 grams of antimony pentachloride in about twice its volume of chloroform, and after surrounding the flask containing this solution with ice, let fall drop by drop 7 grams, the calculated quantity, of water. Again, in this experiment, no hydrochloric acid was given off. The mixture remained at first liquid, but when placed in a vacuum desiccator over sulphuric acid and paraffin, there separated slowly a hard crystalline mass, which was quite insoluble in chloroform. Two chlorine determinations made after washing the substance with chloroform agree with the formula $SbCl_5H_8O_4$.

1. 0·3963 gram substance gave 0·7696 AgCl.
2. 0·3414 „ „ 0·6530 AgCl.

	Calculated for $SbCl_5H_8O_4$.	Found. I.	Found. II.
Cl	47·77	48·04	47·31

Thus besides the monohydrate of antimony pentachloride a tetrahydrate also exists, the latter being easily prepared from a chloroform solution of the former by the action of water, and differing from the monohydrate among other things in being insoluble in chloroform.

From the foregoing evidence it appears that antimony oxychloride, $SbOCl_3$, is certainly not formed by the action of water on antimony pentachloride; but if equal molecules of these substances are allowed to react, the compound $SbCl_5H_2O$ is formed, which we have called antimony pentachloride monohydrate. This product is most con-

veniently formed when water acts on chloroform solution of antimony pentachloride, without setting free hydrochloric acid, according to the equation—

$$SbCl_5 + H_2O = SbCl_5H_2O.$$

When one brings together weights equivalent to 1 mol. of antimony pentachloride and 4 mols. of water, the tetrahydrate of antimony pentachloride is formed, as described by R. Weber. We must put aside Daubrawa's contradiction of the facts of R. Weber, and strike Daubrawa's hypothetical antimony oxychloride, $SbOCl_3$, from the list of the known antimony compounds.

The Reaction of Antimony Pentachloride and Oxalic Acid.

As has already* been remarked, our research on the chlorides of antimony sprung originally from the wish to find out if the reaction of anhydrous oxalic acid and antimony pentachloride was analogous to that of phosphorus pentachloride, forming an antimony oxychloride, $SbOCl_3$, corresponding to the oxychloride of phosphorus. The knowledge of the action of water on antimony pentachloride, forming mono- and tetra-hydrates, increased the interest in the attempt to discover the action of oxalic acid on the same body.

On mixing equal molecular weights of pure anhydrous oxalic acid and antimony pentachloride, a violent development of hydrochloric acid takes place, the mixture forming a nearly solid white mass. The generation of hydrochloric acid soon ceases. On heating to about 150° decomposition begins again, carbonic dioxide and hydrochloric acid being given off, the mass becoming gradually liquid. This clearly showed that the reaction ran in two stages. In the case of the monohydrate we had obtained our object so quickly by the use of chloroform, that we did not pursue the direct action of antimony pentachloride on oxalic acid further, but substituted a cooled solution of 35·5 grams of antimony pentachloride in 83·3 grams of chloroform, with 10·6 grams of anhydrous oxalic acid. The reaction commenced in the cold; at first hydrochloric acid mixed with a small quantity of carbon dioxide was given off, but soon only hydrochloric acid; gradually a considerable amount of a white crystalline body fell out of solution. After the development of hydrochloric acid had ceased, we heated the product of the reaction, dissolving the greater part of the crystals. We filtered hot, and beautiful transparent colourless crystals separated from the filtrate, which we had placed in a desiccator over sulphuric acid and paraffin. The residue, insoluble in the hot chloroform solution, weighed 4·9 grams, and consisted chiefly of unaltered oxalic acid. The quantity of hydro-

* 'Chem. Soc. Journ.,' vol. 49, p. 708.

chloric acid collected was 4·7 grams, while 8·5 grams should have been found had the reaction taken place according to the equation—

$$(COOH)_2 + SbCl_5 = SbCl_3O + CO_2 + CO + 2HCl.$$

This reaction was, however, impossible, owing to the small quantity of carbon dioxide given off. The quantity of hydrochloric acid found indicated that two molecules of antimony pentachloride had reacted with one of oxalic acid. The tabular crystals from the chloroform solution melted at from 148·5° to 149°, decomposing at a somewhat higher temperature. The values found by analysis corresponded to the formula $Sb_2Cl_8C_2O_4$.

1. 0·4860 gram substance gave 0·2637 Sb_2S_3.
2. 0·2647 ,, ,, 0·1421 Sb_2S_3.
3. 0·1444 ,, ,, 0·2670 AgCl.
4. 0·2261 ,, ,, 0·4174 AgCl.
5. 0·8117 ,, ,, 0·1950 $C_2O_4Ca + H_2O$.
6. 0·2522 ,, ,, 0·0589 $C_2O_4Ca + H_2O$.
7. 0·2956 ,, ,, 0·0415 CO_2 and 0·0160 H_2O } Combustion with
8. 0·8777 ,, ,, 0·1162 CO_2 and 0·0162 H_2O } lead chromate.

	Calculated for $Sb_2Cl_8C_2O_4$.	Found. 1.	2.	3.	4.	5.	6.	7.	8.
Sb ..	39·61	38·93	38·52	—	—	—	—	—	—
Cl...	46·10	—	—	45·74	45·64	—	—	—	—
C ...	3·89	—	—	—	—	—	—	3·83	3·61
C_2O_4	14·28	—	—	—	—	14·47	14·07	—	—
H...	0·0	—	—	—	—	—	—	0·59	0·20

The compound, $Sb_2Cl_8C_2O_4$, is formed according to the equation—

$$(COOH)_2 + 2SbCl_5 = C_2O_4Sb_2Cl_8 + 2HCl.$$

Proceeding exactly as described above, but taking one molecule of oxalic acid to two of antimony pentachloride, *i.e.*, twice the quantity, almost the entire product is soluble in chloroform.

37·2 grams $SbCl_5$ dissolved in 55 grams $CHCl_3$ and
5·5 grams $(COOH)_2$ gave
4·3 grams of HCl, the calculated quantity being
4·8 grams.

It is necessary to have a good return-flow condenser in order to avoid a considerable quantity of chloroform distilling into the weighed water, used for collecting the hydrochloric acid. On mixing $Sb_2Cl_8C_2O_4$ with warm water, it is decomposed, setting oxalic acid free. This may be easily determined after removing the antimony from the acid solution. The following constitutional formula seems

most simply to explain the formation and decomposition of this new compound:—

$$\text{I.}\quad \begin{array}{l} COOSbCl_4 \\ | \\ COOSbCl_4 \end{array},$$

oxalic acid in which the hydrogen atoms are replaced by the univalent radical $Sb'Cl_4$. Considering the fact that the compound does not unite with a second molecule of oxalic acid, the formula—

$$\text{II.}\quad \begin{array}{l} COO \\ | \\ COO \end{array}\!\!>SbCl_3SbCl_5$$

does not seem at all probable. According to formula I. one can compare the compound with diammonium oxalate, and designate it as ditetrachlorstibonium oxalate, or as we prefer, look on it as the mixed anhydride of oxalic acid and the yet unknown acid, $SbCl_4OH$.

As a result of these simple experiments we can understand the entirely different behaviour of antimony and phosphorus pentachlorides towards the carbon compounds containing oxygen and hydrogen. Antimony pentachloride unites, as we have proved, with water. Phosphorus pentachloride decomposes water. Antimony pentachloride has no inclination to change chlorine for oxygen. Phosphorus has this inclination in an extraordinary degree. Phosphorus pentachloride attacks hydroxyl or ketone groups, replacing oxygen by respectively one or two atoms of chlorine, being itself converted into oxychloride. Antimony pentachloride, on the other hand, reacts on the hydrocarbon residue, substituting chlorine for hydrogen, and itself becoming antimony trichloride.

Phosphorus pentachloride acts similarly to antimony pentachloride, substituting chlorine for hydrogen in those organic compounds which contain no oxygen, or oxygen in such firm combination with carbon as not to be available for the formation of phosphorus oxychloride.

Antimony pentachloride may react as phosphorus pentachloride on compounds similar to oxalic acid, containing no hydrogen attached to carbon which can be replaced by chlorine. The compound $(COOSbCl_4)_2$ is of especial theoretical interest, as showing the process of the reaction of phosphorus pentachloride on substances containing the hydroxyl group. The first stage of the reaction consists, evidently, of the formation of compounds analogous in composition to the body $(COOSbCl_4)_2$.

If, however, the oxygen of a hydroxyl group is held in loose combination, the formation of phosphorus oxychloride and the substitution of chlorine take place simultaneously. What, however, will happen when the substitution of oxygen is difficult, as in phenol or the aromatic oxyacids? Attempts to answer this question are now

in progress in the laboratory of the Chemical Institute of the University of Bonn, and we anticipate that the result will be the preparation of bodies having the general formula $R'OPCl_4$.

XII. "Note on the Electrodeposition of Alloys and on the Electromotive Forces of Metals in Cyanide Solutions." By SILVANUS P. THOMPSON, D.Sc., B.A. Communicated by Professor G. CAREY FOSTER, F.R.S. Received May 12, 1887.

It is known that the electrodeposition of such alloys as brass, bronze, and German silver is not practicable from mixed solutions of the sulphates or chlorides of the constituent metals, but can be accomplished by using cyanide solutions or neutral solutions containing cyanide of potassium in excess, thereby apparently departing from the law of Berzelius that out of a solution of mixed metals the least electropositive metal is deposited first.

To ascertain the cause of these facts the author has investigated—

(*a.*) The electromotive forces of a number of metals in aqueous solutions of cyanide of potassium.

(*b.*) The dependence of these electromotive forces, in particular those of copper and zinc, upon the degree of concentration of the solution.

(*c.*) The variation of the electromotive forces of copper and zinc in a standard solution of cyanide of potassium at varying temperatures.

(*d.*) The electromotive forces of zinc and copper in a "brassing" solution consisting of the mixed cyanides of zinc and copper, having excess of cyanide of potassium present, and their variation at different temperatures.

It is found that the effect of higher concentration of the cyanide solutions is invariably to increase the electromotive force of copper more than it increases that of zinc.

In a cold dilute solution of cyanide of potassium the electromotive force of zinc against carbon is 1·158 volt, while that of copper against carbon is 0·948 volt, or zinc is 0·210 volt higher than copper. In a boiling saturated solution of cyanide of potassium, the electromotive force of zinc against carbon is 0·768 volt, and that of copper against carbon is 1·300 volt; or copper is 0·532 volt higher than zinc.

It is therefore possible to construct a voltaic battery containing one metal only, namely copper, and one electrolyte only, namely an aqueous solution of cyanide of potassium, kept hot at the anode and cold at the cathode of the cell.

In cyanide solutions containing about the following number of